

DOI:10.1002/ejic.201500077

Ferrocenyl–Bipyridinium Cations and Their Platinum Complexes Related to Viologens – Preparation, Redox Properties, and Crystal Structures

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Keywords: Metallocenes / Viologens / Platinum / Donor-acceptor systems / Electrochemistry

 $N-R^1-N'-R^2-4,4'$ -Bipyridinium and $N-R^1-4,4'$ -bipyridinium salts containing ferrocenyl substituents were prepared as donor-acceptor compounds (R^1 = ferrocenyl, ferrocenyl-phenyl; R^2 = ferrocenyl, ferrocenylphenyl, phenyl, methyl). Platinum(II)-bridged diferrocene compounds were prepared by using the $N-R^1-4,4'$ -bipyridinium ligands. These compounds display multistage redox properties. The redox potentials of the ferrocenyl and bipyridinium moieties in

Introduction

Donor-acceptor molecules have attracted significant interest in terms of their molecular design towards nonlinear optical properties, functional dyes, electrochromic devices, and photoinduced-electron-transfer systems. Ferrocenes are electron donors that have been widely applied in the fabrication of molecular functional materials.^[1] In particular, diferrocenes bridged by π -conjugated spacers or through coordination bonds have garnered interest because of the electronic communication observed between Fe atoms in the mixed-valent state.^[2,3] Viologens are electron acceptors that undergo two-step redox processes and have been used as redox indicators, in electrochemical devices, and as components of ion-pair compounds.^[4,5] The electronic properties of molecules containing ferrocenes and viologens are of great interest because of their potential applications as donor-acceptor multistage redox systems. To this end, several ferrocene-viologen compounds have been prepared, and their electrochromic properties,^[6] redox control of internal rotations,^[7] nonlinear optical activities,^[8]

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500077.

these compounds are independently affected by molecular modifications, which indicates that conjugation between the donor and acceptor moieties is less effective. Single-crystal X-ray diffraction analyses revealed large twist angles between the two moieties in the solid state. The compounds exhibit broad charge-transfer absorption bands in the range 450–800 nm. No electronic communication was observed between the terminal ferrocenes in the diferrocene complexes.

and solid-state physical properties have been evaluated.^[9] Recently, several other ferrocene-based donor–acceptor molecules have been reported.^[10]

Herein, we report the preparation of a series of diferrocenyl– and ferrocenyl–bipyridinium cations, shown in Figure 1. Hexafluorophosphate was used as the counter anion. The salts of viologen-bridged diferrocenes $[1x][PF_6]_2$ as well as mono-ferrocenyl viologen derivatives $[2x][PF_6]_2$ and



Figure 1. Structures of ferrocenyl-bipyridinium cations investigated in this study.



 $[3x][PF_6]_2$ were prepared (x = a, b). Molecules with and without phenylene groups are subsequently denoted as series **a** and **b**, respectively. Furthermore, platinum-bridged diferrocenes $[5x][PF_6]_4$ were prepared from ferrocenyl bipyridines $[4x][PF_6]$ to investigate the electronic properties of metal-bridged diferrocenes. The crystal structure and redox properties of $[3a][PF_6]_2$ have recently been reported.^[7a]

Results and Discussion

Preparation and Properties

 $[1x][PF_6]_2-[3x][PF_6]_2$ and $[4x][PF_6]$ (x = a, b) were prepared by reaction of the corresponding 2,4-dinitrophenylpyridinium salts with aminoferrocene or ferrocenylaniline (Scheme 1, a). Platinum complexes $[5x][PF_6]_4$ were prepared by the reaction of $[4x][PF_6]$ with *trans*- $[Pt(NH_3)_2(H_2O)_2]^{2+}$ (Scheme 1, b). All prepared complexes are air-stable, although the compounds in the **b** series are unstable upon exposure to visible light in solution. The presence of the phenylene spacer in the **a** series resulted in improved stability towards light. However, $[1a][PF_6]_2$ and $[2a][PF_6]_2$ are photosensitive.



Scheme 1. Synthesis of (a) $[1x]^{2+}$, (b) $[2x]^{2+}$ and $[3x]^{2+}$, and (c) $[4x]^+$ and $[5x]^{4+}$ (x = a, b). Counter anions (Cl⁻ or PF₆⁻) have been omitted for clarity.

Electronic Spectra

The UV/Vis absorption spectra of $[1x][PF_6]_2-[3x][PF_6]_2$, $[4x][PF_6]$, and $[5x][PF_6]_4$ in acetonitrile are shown in Figure 2. These compounds exhibit weak and very broad absorption bands in the visible region ($hv_{max} = 15100-$ 19800 cm⁻¹; $\lambda_{max} = 500-660$ nm), which can be attributed to metal-to-ligand charge-transfer (CT) bands,^[11] and their energies are related to the HOMO–LUMO gaps of the compounds. The band intensities are weak, which points to the ineffective conjugation between the donor and acceptor moieties. Spectral data for the CT bands are summarized in Table 1. The energies of the CT bands increased in the order $[1x]^{2+} \approx [2x]^{2+} < [3x]^{2+} < [4x]^+$. The higher CT energy in $[4x]^+$ is in agreement with the higher LUMO energies of bipyridinium derivatives $[4x]^+$ compared to viologen derivatives $[1x]^{2+}-[3x]^{2+}$. Protonation of the pyridine moiety in $[4x]^+$, achieved by addition of trifluoromethane sulfonic acid in acetonitrile, resulted in UV/Vis absorption spectra that are almost identical to those of $[3x]^{2+}$ (Figure S1).



Figure 2. UV/Vis absorption spectra of $[1x][PF_6]_2-[3x][PF_6]_2$, $[4x][PF_6]$, and $[5x][PF_6]_4$ (x = a, b) in acetonitrile.

Table 1. Spectral data for CT bands in acetonitrile.

	$v_{\rm max} [{\rm cm}^{-1}]$	$\varepsilon_{\rm max} [{ m M}^{-1} { m cm}^{-1}]$	$\Delta v_{1/2} [{ m cm}^{-1}]$
$[1a][PF_6]_2$	17200	2890	7120
$[2a][PF_6]_2$	17200	2460	7450
$[3a][PF_6]_2$	18000	1740	6970
[4 a][PF ₆]	19800	2380	5290
[5a][PF ₆] ₄	18700	3500	6750
$[1b][PF_6]_2$	15100	3800	5360
$[2b][PF_6]_2$	15300	3700	5020
$[3b][PF_6]_2$	15900	2320	4290
[4b][PF ₆]	17900	2040	4870
[5b][PF ₆] ₄	16600	5020	5350

The CT energies of $[5x]^{4+}$ are in between those observed for ligands $[4x]^+$ and $[1x]^{2+}-[3x]^{2+}$. This observation is consistent with a decrease in LUMO energy upon metal coordination. A similar phenomenon was reported for metal complexes with bipyridinium or pyridine ligands.^[12–14] The ¹H NMR signals corresponding to the bipyridinium protons in the platinum complexes also appear at chemical shifts in between those observed for $[4x]^+$ and viologen derivatives $[1x]^{2+}-[3x]^{2+}$. Upon comparison of series **a** and **b**, the CT energies in the former compounds are on average 2×10^3 cm⁻¹ higher than those in the latter compounds. This is probably due to the conjugation between the donor and acceptor moieties, which is disrupted by the phenylene group in series **a**, as observed in the crystal structures (vide infra). The absorptions at $hv_{\text{max}} = 2.6 \times 10^4 - 3.1 \times 10^4 \text{ cm}^{-1}$ $(\lambda_{\text{max}} = 320 - 380 \text{ nm})$ can be attributed to $\pi - \pi^*$ transitions, and their energies increase in the order $[\mathbf{1x}]^{2+} < [\mathbf{2x}]^{2+}$ $< [\mathbf{3x}]^{2+} < [\mathbf{4x}]^+$. The energies for series **b** are higher than those for series **a**, which is consistent with the length of conjugation. The absorption bands in the platinum complexes again appear at wavelengths in between those observed for $[\mathbf{4x}]^+$ and the viologen derivatives $[\mathbf{1x}]^{2+} - [\mathbf{3x}]^{2+}$.

Crystal Structures

The crystal structures of $[1a][PF_6]_2$, $[3a][PF_6]_2$, $[3b][PF_6]_2$, [4a]Cl, $[4b][PF_6]_2$, and $[5a][PF_6]_4$ were determined by singlecrystal X-ray diffraction analyses; the structure of [3a]- $[PF_6]_2$ has been reported.^[7a] In all crystals, the counter anions were located in the vicinity of the pyridinium nitrogen and formed cation–anion pairs $[N(1)\cdots P 4.2-4.8 \text{ Å} \text{ and} N(1)\cdots Cl 3.4 \text{ Å}]$. The positions of the chlorine anions in [4a]Cl were disordered. The Cp (cyclopentadienyl) rings in $[1a]^{2+}$ and $[4a]^+$ exhibited rotational disorder. The amine ligands in $[5a][PF_6]_4$ exhibited a twofold disorder in a 0.6:0.4 ratio.

The molecular structures of the cations in these salts are shown in Figure 3. In $[1a]^{2+}$, the terminal ferrocenes are twisted by 180° with respect to one another and the intramolecular Fe····Fe distance is 20.8 Å. The other compounds also exhibited twisted structures. The dihedral angles between adjacent rings in these compounds and related molecules are summarized in Table 2. The central bipyridinium moieties are planar in $[1a]^{2+}$ and $[5a]^{4+}$, and they are twisted by approximately 15-40° in the other compounds (angle A in Scheme 2). The pyridinium rings in dialkyl viologen dications are often coplanar.^[5b] It should be noted that the angles between the pyridinium ring and the adjacent ring (angle B) are generally large (40–55°). The balance between ortho-hydrogen repulsion and electronic conjugation determines the twist angle; the latter effect is often small because of the large differences in orbital energies between the two moieties.



Figure 3. ORTEP drawings of the molecular structures of the cations in (a) $[1a][PF_6]_2$, (b) $[3a][PF_6]_2$, (c) $[3b][PF_6]_2$, (d) [4a]Cl, (e) $[4b][PF_6]_2$, and (f) $[5a][PF_6]_4$. The disorder of the Cp rings in $[1a]^{2+}$ and $[4a]^+$ is displayed in gray. Hydrogen atoms have been omitted for clarity.



Scheme 2.

The coordination structure of $[5a]^{4+}$ was confirmed by X-ray diffraction analysis (Figure 3, f). This molecule also exhibits large twist angles (Angle B $\approx 40^{\circ}$). The structure of $[5b]^{4+}$ was also confirmed (Figure S2), but the quality of the data is unsatisfactory.^[15]

Redox Potentials

The redox potentials of the compounds were measured by using cyclic voltammetry (CV) and are summarized in

	Angle A [°]	Angle B [°]	Angle C [°]	
Viologens				
[1a] [P F ₆] ₂	0	41.1(2)	9.8(3)	
$[3a][PF_6]_2$	31.1(3)	44.4(3)	9.1(3)	
[3b][PF ₆] ₂	30.95(7)	32.11(8)		
<i>N</i> , <i>N</i> '-Diphenyl-4,4'-viologen ^[b,c]	37.7	37.4(2)		
<i>N</i> , <i>N</i> '-Bis(4-cyanophenyl)-4,4'-viologen ^[d,e]	0	38.8		
N,N'-Bis(4-fluorophenyl)-4,4'-viologen ^[d,f]	0	54.3		
Bipyridinium monocations				
[4 a]Cl	15.09(15)	45.9(1)	21.6(1)	
[4b][PF ₆]	19.3(1)	37.0(1)		
<i>N</i> -Phenyl-4,4'-bipyridinium chloride ^[g]	19.8	39.7		
[5a][PF ₆] ₄	0.7(8)	39.7(9)	5.7(10)	

Table 2. Dihedral angles between adjacent rings in the bipyridinium salts.^[a]

[a] Definition of the dihedral angles is shown in Scheme 2. [b] Dichloride salt. [c] Ref.^[5b] [d] Tetracyanoquinodimethanide (TCNQ) salts. [e] Ref.^[5c] [f] Ref.^[5d] [g] Ref.^[13]



	Eox			E _{red1}			E _{red2}			
	$E_{\rm pc}$	$E_{\rm pa}$	$E_{1/2}$	$E_{\rm pc}$	$E_{\rm pa}$	$E_{1/2}$	$E_{\rm pc}$	$E_{\rm pa}$	$E_{1/2}$	$\Delta E^{[b]}$
$[1a][PF_6]_2^{[c]}$	0.09	0.00	0.05	-0.78	-0.63	-0.71	-1.07	-0.94	-1.01	0.30
$[1a][PF_6]_2^{[d]}$	0.23 ^[g]	0.15	0.19	-0.40	-0.48	-0.44	-0.97	-1.05	-1.01	0.57
$[1b][PF_6]_2^{[c]}$	_	_[h]	_	-0.74	-0.67	-0.71	-1.06	-1.00	-1.03	0.32
$[1b][PF_6]_2^{[d]}$	0.55	0.41	0.48	-0.40	-0.50	-0.45	-1.01	-1.15	-1.08	0.63
$[2a][PF_6]_2^{[c]}$	0.15	0.06	0.11	-0.65	-0.72	-0.69	-0.92	-1.00	-0.96	0.27
$[2b][PF_6]_2^{[c]}$	_	0.45	_	-0.66	-0.73	-0.70	-0.95	-1.03	-0.99	0.29
$[3a][PF_6]_2^{[c,g]}$			$0.07^{[g]}$		_	$-0.82^{[g]}$		_	$-1.14^{[g]}$	0.34
$[3a][PF_6]_2^{[e]}$	0.03	0.12	0.08	-0.82	-0.72	-0.77	-1.15	-1.06	-1.10	0.33
$[3b][PF_6]_2^{[c]}$	_	0.46 ^[f]	_	-0.83	-0.76	-0.80	-1.17	-1.11	-1.14	0.34
$[4a][PF_6]^{[c]}$	0.02	0.11	0.07				$-1.23^{[f]}$	_	_	
[4b][PF ₆] ^[c]	_	0.43 ^[f]	_				$-1.25^{[f]}$	_	_	
$[5a][PF_6]_4^{[c]}$	0.06	0.13	0.10				$-1.02^{[f]}$	_	_	
[5b][PF ₆] ₄ ^[c]	_	_[h]	-				$-1.06^{[f]}$	-	-	

Table 3. Redox potentials (in V vs. [FeCp₂]^{0/+}).^[a]

[a] Scan rate of 100 mVs⁻¹ at a platinum working electrode. [b] $\Delta E = E_{red1} - E_{red2}$. [c] 0.1 M Bu₄NClO₄ in DMF. [d] 0.1 M Bu₄N[B-(C₆F₅)₄] in CH₂Cl₂. [e] 0.1 M Bu₄NClO₄ in MeCN. [f] Irreversible. [g] Ref.^[7a] The potentials (referenced vs. Ag/Ag⁺) were transposed to those referenced vs. [FeCp₂]^{0/+} by subtracting 0.4 V. [h] Not detected.

Table 3. $[1x]^{2+}$ – $[3x]^{2+}$ each exhibit one redox wave for the ferrocenyl moiety (E_{ox}) and two redox waves (E_{red1} and E_{red2}) for the viologen moieties. The voltammogram of $[1a]^{2+}$, recorded in DMF by using Bu₄NClO₄ as the electrolyte, is shown in Figure 4a. Plausible redox processes of $[1x]^{2+}$ are illustrated in Figure 5. $[4x]^+$ exhibits one redox wave for the ferrocenyl moieties and one redox wave for the bipyridinium moiety. The HOMO–LUMO gap of the cations corresponds to the difference between the redox potential of the ferrocenyl moiety (E_{ox}) and the first redox potential of the viologen moiety (E_{red1}). Therefore, the CV results are consistent with the order of the CT energies ($1x \approx 2x < 3x < 5x < 4x$), as mentioned previously. The electrochemical results suggest that the HOMO–LUMO gap in series **b** is larger than that in series **a**, whereas the CT energi



Figure 4. Cyclic voltammograms of (a) $[1a]^{2+}$ in DMF containing 0.1 M Bu₄N[ClO₄], (b) $[1a]^{2+}$ in CH₂Cl₂ containing 0.1 M Bu₄N[B(C₆F₅)₄], and (c) $[1b]^{2+}$ in CH₂Cl₂ containing 0.1 M Bu₄N[B(C₆F₅)₄]. Half-wave potentials are also shown.

gies in series **a** are higher than those in series **b** (vide ante). This is possibly due to the disrupted conjugation.



Figure 5. Plausible multi-stage redox processes of $[1a]^{2+}$ (n = 1) and $[1b]^{2+}$ (n = 0).

Substituent effects on the electrochemical properties of viologen moieties have been extensively studied, and the studies reveal a linear correlation between $E_{\rm red1}$ and $E_{\rm red2}$.^[4e] Figure 6 shows a plot of the redox potentials for the viologen moieties in $[1x]^{2+}$ – $[3x]^{2+}$, which is in agreement with the reported correlation. Both $E_{\rm red1}$ and $E_{\rm red2}$ increase in the order $[3x]^{2+} < [1x]^{2+} < [2x]^{2+}$. The substituent effects on the redox potentials for the viologens exhibit a correlation with the σ^* constants introduced by Taft.^[4e] Figure 7 shows the redox potentials of $[1b]^{2+}$ – $[3b]^{2+}$ plotted as a function of the sum of the Taft σ^* constants of the two



substituents. The value of 0.36 was used as the σ^* constant for the ferrocenyl group.^[16] The data are consistent with the previously reported correlation.^[17]



Figure 6. Correlation of the redox potentials for the viologen moieties ($E_{\text{red}1}$ and $E_{\text{red}2}$, referenced vs. $[\text{FeCp}_2]^{0/+}$) in $[\mathbf{1x}]^{2+}-[\mathbf{3x}]^{2+}$ ($\mathbf{x} = \mathbf{a}, \mathbf{b}$). The dashed line represents the correlation reported in ref.^[4e] ($\mathbf{MV}^{2+} = N, N'$ -dimethyl viologen, PhV²⁺ = N, N'-diphenyl viologen).^[17]



Figure 7. Plots of the redox potentials (E_{red1} and E_{red2}) for viologens $[1b]^{2+}-[3b]^{2+}$ as a function of the sum of the Taft σ^* constants of the two substituents. The solid lines represent the correlations determined from the data of various substituted viologens (ref.^[4e]).

The presence of the phenylene group influenced the redox potentials of the ferrocenyl moiety. The oxidation potentials in $[1a]^{2+}-[4a]^+$ were observed at 0-0.1 V as reversible waves, whereas those in $[1b]^{2+}-[4b]^+$ were observed at approximately 0.45 V as irreversible waves. However, the redox potentials of the bipyridinium moieties in $[1a]^{2+}-[4a]^+$ were almost identical to those observed in $[1b]^{2+}-[4b]^+$. Likewise, the redox potentials of the ferrocenyl moieties were nearly independent of the acceptor moieties; those in $[1x]^{2+}$ - $[3x]^{2+}$ were almost identical to those in $[4x]^+$. These results indicate that the ferrocenyl and viologen moieties display electrochemically independent behavior and that the conjugation between the two moieties is disrupted. This is consistent with the dependence of the redox potentials of the viologens on the Taft σ^* constants, which relate to purely inductive effects and are free from resonance effects. On the basis of the electrochemical features of viologens, Monk postulated that the twist angle in an

aryl-substituted viologen disrupts the conjugation between the aryl and viologen moieties and that resonance effects are marginalized.^[18] Our study proves this by the electrochemical investigation of the redox potentials of ferrocenyl substituents in the present compounds. A similar phenomenon was recently reported for ferrocene-tetracyanobutadiene donor–acceptor derivatives, in which a modification of the acceptor substituent significantly affected the reduction potentials of the acceptor moiety but only slightly affected the oxidation potential of the ferrocene unit.^[1a]

Redox Properties of Diferrocenyl Compounds

Diferrocenyl compounds are interesting because of the electronic communication between the ferrocenyl units.^[2] The ferrocenyl moieties in $[1a]^{2+}$, however, exhibited a onestep oxidation wave in DMF (with Bu₄NClO₄ as an electrolyte), which indicates that there is no electronic communication between the two ferrocenium units (Figure 4, a). The peak of the oxidation wave of the ferrocenyl moieties (twoelectron redox process) was nearly twice as high as those of the reduction waves of the viologen moieties (one-electron redox processes). The redox potentials were also measured in CH₂Cl₂ by using (Bu₄N)[B(C₆F₅)₄] as an electrolyte (Figure 4, b). $[1a][PF_6]_2$ became soluble in CH_2Cl_2 in the presence of this electrolyte. In this solvent, the redox waves for the ferrocenyl moieties, although not fully reversible, also appeared as one-step oxidation waves. A comparison of the voltammograms (Figure 4a and Figure 4, b) obtained $\{electrolyte: Bu_4N[ClO_4]\}\$ and CH_2Cl_2 in DMF $\{\text{electrolyte: } (Bu_4N)[B(C_6F_5)_4]\}$ indicates that the first redox potential of the viologen moieties shows a significant positive shift of approximately 0.3 V in CH₂Cl₂. However, the other redox processes were only slightly affected. A similar effect was also observed for $[1b]^{2+}$ (Figure 4, c). The observed solvent and electrolyte dependence is due to the higher thermodynamic stability of the viologen radical cation in non-polar solvents^[19] and also due to the limited ion pairing with the electrolyte because of the use of the weakly-coordinating $[B(C_6F_5)_4]$ anion.^[20] The redox potentials of the compounds in DMF were almost independent of the electrolyte. In acetonitrile, the redox peaks for the acceptor moieties of the compounds were irreversible, which can be attributed to the poor solubility of the reduced species in the solvent.

The redox potential for the ferrocenyl moieties (E_{ox}) in $[5a]^{4+}$ (0.10 V) is comparable to the potentials found for $[1a]^{2+}-[4a]^+$ (0.05–0.11 V). The ferrocenyl moieties exhibited a one-step oxidation wave, which indicates no electronic communication. We could not observe the oxidation peak for $[5b]^{4+}$ because of decomposition. The redox potentials of the bipyridinium moieties in $[5x]^{4+}$ are located in between those of $[4x]^+$ and the viologen derivatives $[1x]^{2+}-[3x]^{2+}$; the first reduction potentials of the bipyridinium moieties in the order $[4a]^+$ ($E^{1/2} = -1.2 \text{ V}$) $\leq [5a]^{4+}$ (-1.0 V) $\leq [3a]^{2+}$ (-0.8 V), and $[4b]^+$ (-1.3 V) $\leq [5b]^{4+}$ (-1.1 V) $\leq [3b]^{2+}$ (-0.8 V) (Table 3). A sim-



earing pyreral metalmunication N,N'-**Bisferrocenyl**-4,4'-**bipyrid** ([1b][PF₆]₂): This compound **FULL PAPER**

ilar tendency was reported for metal complexes bearing pyridine or pyridinium ligands.^[12-14] There are several metalbridged diferrocenes that exhibit electronic communication between the ferrocenes in the one-electron-oxidized state through the metal ion.^[2] Several metal complexes with Nmethyl-4,4'-bipyridinium ligands have been reported,^[14,21] of which a trinuclear Ru^{II} complex exhibits electronic communication between the bipyridinium moieties through the metal ion.^[21] However, $[5x]^{4+}$ does not display any observable electronic communication between the ferrocene or viologen moieties. In the trinuclear Ru^{II} complex, the orbitals of the ligands and the bridging moieties overlap,^[21] which enables electronic communication between the ligands. In $[1x]^{2+}$ and $[5x]^{4+}$, however, orbital overlap through the bridging moieties is ineffective because of the large energy difference between the bridging moieties and the redox centers. The long distance between the redox centers may also contribute to the absence of electronic communication.

Experimental Section

General: ¹H NMR spectra were recorded with a JEOL JNM-ECL-400 spectrometer. IR spectra were recorded with a JASCO FT-IR 230 spectrometer by using KBr pellets or with a Shimadzu Prestige-21 FTIR-8400S equipped with an AIM-8800 microscope in the 4000–400 cm⁻¹ range. UV/Vis spectra were recorded with a JASCO V-570 UV/Vis/NIR spectrometer or with a Shimadzu MultiSpec-1500 spectrometer. Cyclic voltammograms were recorded by using an ALS/chi electrochemical-analyzer (model 600A). The redox potentials were measured at a scan rate of 0.1 V s⁻¹ in DMF containing 0.1 M *n*Bu₄NClO₄ or in dichloromethane containing 0.1 M (*n*Bu₄N)[B(C₆F₅)₄]. An Ag/Ag⁺ reference electrode and a platinum working electrode were used, and the potentials were referenced to the [Fe(C₅H₅)₂]^{0/+} couple.

Synthesis: All reactions were carried out under a nitrogen atmosphere. Syntheses of all compounds were carried out in the absence of light, and the products were handled under a red lamp. Aminoferrocene, dichlorobis(triphenylphosphine)palladium(II), and *trans*-diamminedichloroplatinum(II) were purchased from TCI. N,N'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium, N-(2,4-dinitrophenyl)-N'-methyl-4,4'-bipyridinium, and N-(2,4-dinitrophenyl)-N'-methyl-4,4'-bipyridinium dichloride salts were prepared by using literature methods,^[22] and they were converted into the corresponding hexafluorophosphate salts by anion exchange in methanol by using NH₄PF₆.

N,*N*'-Bis(4-ferrocenylphenyl)-4,4'-bipyridinium Bis(hexafluorophosphate) ([1a][PF₆]₂): A methanol solution (10 mL) of 4-ferrocenylaniline^[23] (70 mg, 0.25 mol) was added dropwise to N, N'-bis-(2,4-dinitrophenyl)-4,4'-bipyridinium bis(hexafluorophosphate) (100 mg, 0.13 mmol), and the resulting solution was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether and dissolved in methanol. After addition of ether, the solution was left overnight in a refrigerator (ca. -10 °C). A violet powder of the desired compound $[1a][PF_6]_2$ precipitated (95 mg, 9.8×10^{-2} mmol, 75% yield). IR: v = 1632, 1593, 1524, 1490, 1422, 1342, 1285, 1196, 1105, 1003, 887, 829 cm⁻¹. ¹H NMR ([D₆]DMSO): δ = 9.73 (d, J = 5.2 Hz, 4 H), 9.09 (d, J = 6.4 Hz, 4 H), 7.92 (m, 8 H, C₆H₄), 5.03 (m, 4 H, α -C₅ H_2), 4.52 (m, 4 H, β -C₅ H_2), 4.10 (s, 10 H, C₅ H_5) ppm. $C_{42}H_{34}F_{12}FeN_2P_2$ (912.51): calcd. C 52.09, H 3.54, N 2.89; found C 51.49, H 3.62, N 2.54.

N,*N*'-**Bisferrocenyl-4,4**'-**bipyridinium Bis(hexafluorophosphate)** ([1b][PF₆]₂): This compound was prepared as described for [1a][PF₆]₂ by using *N*,*N*'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium bis(hexafluorophosphate) (10 mg, 1.3×10^{-2} mmol) and aminoferrocene (10 mg, 2.5×10^{-2} mmol), and the product was obtained as a violet powder (10 mg, 1.2×10^{-2} mmol, 92% yield). IR: $\tilde{v} = 1614$, 1549, 1537, 1447, 1352, 879 cm⁻¹. ¹H NMR ([D₆]DMSO): $\delta = 9.65$ (d, *J* = 6.8 Hz, 4 H), 8.72 (d, *J* = 7.2 Hz, 4 H), 5.58 (m, 4 H, α-C₅H₂), 4.80 (m, 4 H, β-C₅H₂), 4.40 (s, 10 H, C₅H₅) ppm. C₃₀H₂₆F₁₂Fe₂N₂P₂ (816.17): calcd. C 44.15, H 3.19, N 3.43; found C 44.04, H 3.19, N 3.35.

N-Ferrocenylphenyl-*N*'-phenyl-4,4'-bipyridinium Bis(hexafluorophosphate) ([2a][PF₆]₂): *N*-(2,4-dinitrophenyl)-*N*'-phenyl-4,4'-bipyridinium bis(hexafluorophosphate) (90 mg, 1.3×10^{-1} mmol) and ferrocenylaniline (70 mg, 2.0×10^{-1} mmol) were dissolved in methanol (2 mL) and stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether and dissolved in acetonitrile. After addition of ether, the solution was left overnight in a refrigerator. A blue powder of [2a][PF₆]₂ precipitated (95 mg, 1.2×10^{-1} mmol, 93% yield). ¹H NMR ([D₆]DMSO): $\delta = 9.72$ (br., 4 H), 9.08 (br., 4 H), 7.93– 7.83 (br., 9 H, C₆H₄, C₆H₅), 5.03 (s, 2 H, α -C₅H₂), 4.52 (s, 2 H, β -C₅H₂), 4.10 (s, 5 H, C₅H₅) ppm. C₃₂H₂₆F₁₂FeN₂P₂ (784.34): calcd. C 49.00, H 3.34, N 3.57; found C 48.70, H 3.43, N 3.43.

N-Ferrocenyl-*N*'-phenyl-4,4'-bipyridinium Bis(hexafluorophosphate) ([2b][PF₆]₂): This compound was prepared as described for [2a][PF₆]₂ by using *N*-(2,4-dinitrophenyl)-*N*'-phenyl-4,4'-bipyridinium bis(hexafluorophosphate) (90 mg, 1.3×10^{-1} mmol) and aminoferrocene (30 mg, 1.5×10^{-1} mmol), and the product was obtained as a blue powder (56 mg, 7.9×10^{-2} mmol, 61% yield). ¹H NMR ([D₆]DMSO): δ = 9.69 (br., 4 H), 9.02 (br., 2 H), 8.79 (br., 2 H), 7.97–7.82 (br., 5 H, C₆H₅), 5.60 (s, 2 H, α -C₅H₂), 4.80 (s, 2 H, β -C₅H₂), 4.42 (s, 5 H, C₅H₅) ppm. C₂₆H₂₂F₁₂FeN₂P₂ (708.24): calcd. C 44.09, H 3.13, N 3.96; found C 44.73, H 3.28, N 3.83.

N-(4-Ferrocenylphenyl)-N'-methyl-4,4'-bipyridinium Bis(hexafluorophosphate) ([3a][PF₆]₂):^[7a] A methanol solution (20 mL) of 4-ferrocenylaniline (80 mg, 2.9×10^{-1} mmol) was slowly added to N-(2,4-dinitrophenyl)-N'-methyl-4,4'-bipyridinium chloride iodide (100 mg, 2.4×10^{-1} mmol), and the resulting solution was heated at reflux for 12 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether and recrystallized from methanol/diethyl ether to give [3a]ICl (83 mg, 1.4×10^{-1} mmol, 58% yield). A methanol solution (5 mL) of NaPF₆ (38 mg) was added to a methanol solution (5 mL) of [3a]IC1 (100 mg, 1.7×10^{-1} mmol), and the desired compound [3a] [PF₆]₂ precipitated as a violet powder (76 mg, 1.1×10^{-1} mmol, 65% yield). IR: $\tilde{v} = 1443$, 1420, 1280, 1103, 1032, 829, 818 cm⁻¹. ¹H NMR ([D₆]DMSO): δ = 9.69 (d, J = 5.5 Hz, 2 H), 9.31 (d, J = 5.8 Hz, 2 H), 8.93 (d, J = 5.5 Hz, 2 H), 8.87 (d, J = 5.8 Hz, 2 H), 7.93 (d, J = 8.0 Hz, 2 H, C₆ H_4), 7.85 (d, J = 8.0 Hz, 2 H, C₆ H_4), 5.01 (t, J = 1.8 Hz, 2 H, α -C₅ H_2), 4.50 (t, J = 1.8 Hz, 2 H, β -C₅ H_2), 4.45 (s, 3 H, CH₃), 4.09 (s, 5 H, C₅H₅) ppm. C₂₇H₂₄F₁₂FeN₂P₂ (722.27): calcd. C 44.90, H 3.35, N 3.88; found C 44.39, H 3.32, N 3.89.

N-Ferrocenyl-*N*'-methyl-4,4'-bipyridinium Bis(hexafluorophosphate) ([3b][PF₆]₂): A methanol solution (3 mL) of *N*-methyl-*N*'-(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride (19 mg, 4.7×10^{-2} mmol) and 4-aminoferrocene (10 mg, 5.0×10^{-2} mmol) was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in a small amount of meth-



anol. After addition of ether, the solution was left overnight. [**3b**]-Cl₂ precipitated as a black-green powder (19 mg, 4.6×10^{-2} mmol, 98% yield). An aqueous solution of [**3b**]Cl₂ was added dropwise to an aqueous solution of NH₄PF₆, and the desired compound [**3b**][PF₆]₂ precipitated as a black powder (14 mg, 2.2×10^{-2} mmol, 46% yield). IR: $\tilde{v} = 1639$, 1503, 1455, 832, 557 cm⁻¹. ¹H NMR ([D₆]DMSO): $\delta = 9.65$ (d, J = 5.9 Hz, 2 H), 9.28 (d, J = 5.9 Hz, 2 H), 8.82 (d, J = 5.9 Hz, 2 H), 8.66 (d, J = 5.9 Hz, 2 H), 5.57 (s, 2 H, α -C₅H₂), 4.78 (s, 2 H, β -C₅H₂), 4.43 (s, 3 H, CH₃), 4.39 (s, 5 H, C₅H₅) ppm. C₂₁H₂₀F₁₂FeN₂P₂ (646.17): calcd. C 39.03, H 3.12, N 4.34; found C 39.12, H 3.22, N 4.05.

N-(4-Ferrocenylphenyl)-4,4'-bipyridinium Hexafluorophosphate ([4a][PF₆]): An ethanol solution (10 mL) of 4-ferrocenylaniline (200 mg, 7.2×10^{-1} mmol) and N-(2,4-dinitrophenyl)bipyridinium chloride^[12] (82 mg, 2.3×10^{-1} mmol) was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in water and filtered. The filtrate was concentrated by removing the solvent under reduced pressure, and the residue was washed with diethyl ether. The residue was dissolved in a minimum amount of dichloromethane, to which ether was added, and the mixture was left to stand overnight. [4a]Cl precipitated as a violet powder (80 mg, 1.8×10^{-1} mmol, 77% yield). An aqueous solution of KPF₆ was added to an aqueous solution of [4a]Cl, and the desired compound [4a][PF₆] precipitated as a black powder (39% yield). IR: $\tilde{v} = 1638, 1598, 1518, 1409, 832,$ 557 cm⁻¹. ¹H NMR ([D₆]DMSO): $\delta = 9.52$ (d, J = 6.6 Hz, 2 H), 8.78 (d, J = 7.0 Hz, 2 H), 8.16 (d, J = 6.2 Hz, 2 H), 8.91 (d, J =5.9 Hz, 2 H), 7.90 (d, J = 8.8 Hz, 2 H, C₆ H_4), 7.83 (d, J = 8.8 Hz, 2 H, C₆ H_4), 5.00 (t, J = 1.8 Hz, 2 H, α -C₅ H_2), 4.49 (t, J = 1.8 Hz, 2 H, β-C₅H₂), 4.09 (s, 5 H, C₅H₅) ppm. C₂₆H₂₁F₆FeN₂P (562.27): calcd. C 55.54, H 3.76, N 4.98; found C 55.35, H 3.92, N 4.85.

N-Ferrocenyl-4,4'-bipyridinium Hexafluorophosphate ([4b][PF₆]): The compound was prepared as described for [4a][PF₆] by using aminoferrocene (31 mg, 0.15 mmol), *N*-(2,4-dinitrophenyl)bipyridinium chloride (50 mg, 1.4×10^{-1} mmol), and ethanol (3 mL). Anion exchange of the black powder of [4b]Cl (44 mg, 9.9×10^{-2} mmol, 84% yield) with NH₄PF₆ afforded the desired compound [4b][PF₆] as a black powder (37 mg, 7.7×10^{-2} mmol, 78% yield). IR: $\tilde{v} = 1633$, 1410, 835, 557 cm⁻¹. ¹H NMR ([D₆]-DMSO): $\delta = 9.52$ (d, J = 6.6 Hz, 2 H), 8.54 (d, J = 6.2 Hz, 2 H), 8.11 (d, J = 5.1 Hz, 2 H), 8.90 (d, J = 5.1 Hz, 2 H), 5.50 (t, J =1.8 Hz, 2 H, α-C₅H₂), 4.70 (s, J = 1.8 Hz, 2 H, β-C₅H₂), 4.39 (s, 5 H, C₅H₅) ppm. C₂₀H₁₇F₆FeN₂P (486.18): calcd. C 49.41, H 3.52, N 5.76; found C 49.67, H 3.66, N 5.59.

trans- $[Pt(NH_3)_2(3a)_2](PF_6)_4$ ([5a] $[PF_6]_4$): An aqueous solution (1 mL) of silver nitrate (17 mg, 9.4×10^{-2} mmol) was added to *trans*-diamine dichloroplatinum(II) (15 mg, 5.0×10^{-2} mmol), and the resulting solution was stirred at 60 °C for 3 h. After removing silver chloride by filtration, an aqueous solution (4 mL) of [4a]Cl (45 mg, 1.0×10^{-1} mmol) was added to the filtrate, and the resulting solution was stirred at 60 °C for a further 10 d. The solvent was removed under reduced pressure, and the residue was washed with acetonitrile to give [5a][NO₃]₂Cl₂ as a blue-purple powder (54 mg, 4.3×10^{-2} mmol, 86% yield). Aqueous solutions of the product and KPF₆ were mixed and left overnight, and the desired compound [5a] [PF₆]₄ precipitated as a violet powder (37 mg, 2.2×10^{-2} mmol, 52% yield). IR: $\tilde{v} = 1624$, 1523, 1424, 837, 558 cm⁻¹. ¹H NMR $([D_6]DMSO): \delta = 9.66 (d, J = 2.8 Hz, 4 H), 9.09 (d, J = 2.6 Hz, 4$ H), 8.90 (d, J = 2.6 Hz, 4 H), 8.55 (d, J = 2.7 Hz, 4 H), 7.94 (d, J = 3.9 Hz, 4 H, C_6H_4), 7.86 (d, J = 3.9 Hz, 4 H, C_6H_4), 5.01 (s, 4 H, α-C₅H₂), 4.79 (s, 6 H, NH₃), 4.51 (s, 4 H, β-C₅H₂), 4.09 (s, 10 H, C₅H₅) ppm. C₅₂H₄₈F₂₄Fe₂N₆P₄Pt (1643.62): calcd. C 38.00, H 2.94, N 5.11; found C 38.08, H 3.13, N 4.85.

trans-[Pt(NH₃)₂(3b)₂](PF₆)₄ ([5b][PF₆]₄): An aqueous solution (1 mL) of silver nitrate (12 mg, 0.067 mmol) was added to *trans*diamine dichloroplatinum(II) (10 mg, 0.033 mmol), and the resulting solution was stirred at 60 °C for 3 h. Silver chloride was removed by filtration, a methanol solution (1 mL) of [4b][PF₆] (45 mg, 9.3×10^{-2} mmol) was added to the filtrate, and the resulting solution was stirred at 40 °C for 10 h. Water was added, and the solution was filtered. The filtrate was added dropwise to an aqueous solution of KPF₆, and the desired compound [5b][PF₆]₄ precipitated as a blue powder (19 mg, 1.2×10^{-2} mmol, 36% yield). IR: $\tilde{v} = 845$, 560 cm⁻¹. ¹H NMR ([D₆]DMSO): $\delta = 9.61$ (d, J =6.6 Hz, 4 H), 9.05 (d, J = 6.6 Hz, 4 H), 8.63 (d, J = 6.6 Hz, 4 H), 8.50 (d, J = 6.6 Hz, 4 H), 5.54 (s, 4 H, α -C₅H₂), 4.78 (s, 4 H, β -C₅H₂), 4.41 (s, 10 H, C₅H₅) ppm. C₄₀H₄₀F₂₄Fe₂N₆P₄Pt (1491.43): calcd. C 32.21, H 2.70, N 5.63; found C 32.14, H 2.90, N 5.62.

X-ray Crystallography: Single-crystal X-ray diffraction data were collected with a Bruker APEX CCD diffractometer by using $Mo(K_a)$ radiation ($\lambda = 0.71069$ Å). Single crystals of [1a][PF₆]₂, [3a][PF₆]₂, [3b][PF₆]₂, [4a]Cl, and [5b][PF₆]₄ were obtained by vapor diffusion of diethyl ether into acetonitrile solutions of the compounds. Single crystals of [4b][PF₆] were obtained by vapor diffusion of diethyl ether into an acetone solution, and crystals of [5a][PF₆]₄ were obtained by vapor diffusion of chloroform into an acetonitrile solution. The crystals were coated with black ink to prevent photo-degradation. Crystallographic parameters are listed in Table S1. The data for [3a][PF₆]₂ are not included in the table, because the structure was identical to the literature data.^[7a] The structures were solved by direct methods and refined by using SHELX97.^[24] Molecular structures were drawn by using ORTEP-3 for Windows.^[25]

CCDC-265369 (for $[1a][PF_6]_2$), -265370 (for $[3a][PF_6]_2$), -626788 (for $[3b][PF_6]_2$), -265371 (for [4a]Cl), -265372 (for $[4b][PF_6]_2$), and -988487 (for $[5a][PF_6]_4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Change in UV/Vis spectra upon protonation of $[4x]^+$, ORTEP drawing of the molecular structure of $[5b]^{4+}$, cyclic voltammograms of $[1x]^{2+}$ – $[3x]^{2+}$ and $[4x]^+$, and crystallographic parameters.

Acknowledgments

This work was financially supported by KAKENHI from Japan Society for the Promotion of Science (grant number 26104524). The authors thank K. Okazawa and T. Akasaka (Toho University) for their help with X-ray crystallography.

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Received: January 24, 2015 Published Online: March 26, 2015